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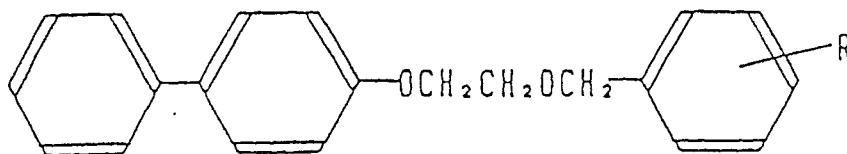
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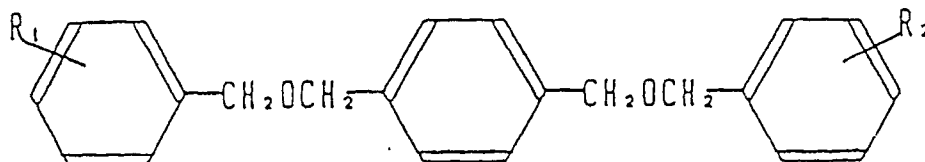
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(54) **Heat-sensitive recorder.**

(57) Disclosed in a heat-sensitive recorder comprising, on a support, a heat-sensitive recording layer containing a leuco compound and an organic acidic substance capable of developing upon reaction with the leuco compound, wherein the heat-sensitive recording layer further contains a compound of the following general formula (I) or (II):



... (I)



... (II)

wherein R represents an alkyl group having 1 to 4 carbon atoms, and R<sub>1</sub> and R<sub>2</sub> each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms. The heat-sensitive recorder has a quite high image density, high practical value and quite excellent storability.

## HEAT-SENSITIVE RECORDER

The present invention relates to an improvement in a heat-sensitive recorder mainly comprising a colorless or light-colored organic dye usually called as a leuco compound and an organic acidic substance capable of developing upon reaction with the leuco compound, such as a phenol compound.

Heat-sensitive recording papers containing the leuco compound and the organic acid are well known from, for example, Japanese Patent Publication for Opposition Purpose (hereinafter referred to as 'J. P. KOKOKU') No. 45-14039. These recording papers are produced on the principle that a thermal energy is applied to the recording layer to soften or to melt the leuco compound, organic acid and a binder and whereby both the color-forming agents are brought into contact with each other to cause a color-forming reaction. Recently these heat-sensitive recording papers are used in the fields of printers and facsimiles. The recording papers have various properties which varies depending on the use. For example, to increase the recording speed, the improvement of the recording device and the color-forming property of the recording paper per se are necessitated.

The color formation is accelerated usually by incorporating a low-melting substance into the recording layer. As the low-melting substances, namely color formation accelerators or sensitizers, urea, phthalic anhydride and acetanilide are used in J. P. KOKOKU No. 43-4160, paraffin wax, carnauba wax, Japan wax, higher fatty acids and higher fatty acid esters are used in Japanese Patent Unexamined Published Application (hereinafter referred to as 'J. P. KOKAI'), No. 48-19231 and salicylic acid, anisic acid, monophenyl phthalate and monobenzyl phthalate are used in J. P. KOKOKU No. 49-17748. Further fatty acid amides are widely used as the color formation-accelerator recently. J. P. KOKOKU No. 51-27599 discloses that when a fatty acid amide is used in combination with a paraffin or micro wax, the sensitizing effect of the fatty acid amide is increased. J. P. KOKAI No. 54-139740 discloses the sensitizing effect of fatty acid amides such as stearamide and oleamide.

Further J. P. KOKAI No. 58-87094 discloses 2-benzyloxynaphthalene and J. P. KOKAI No. 60-82382 discloses p-bezylbiphenyl.

However, the color formation-accelerating effects of the above-described compounds are yet insufficient and techniques of providing more excellent color formation effect have eagerly been demanded.

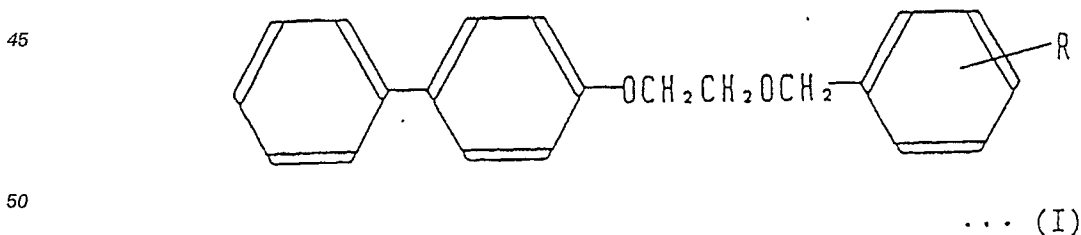
## Summary of the Invention

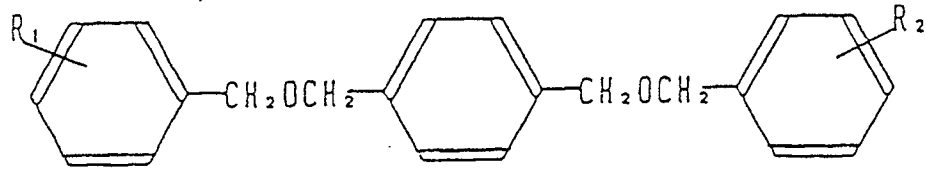
A primary object of the present invention is to provide a heat-sensitive recorder having a color forming effect superior to that of the conventional heat-sensitive recorders.

This and other objects of the present invention will be clear from the following description and Examples.

After investigations of color formation-accelerating effects of various compounds, the inventors have found that specified compounds have excellent properties, particularly image density-increasing effect and that the object of the present invention can be effectively attained with these compounds. The present invention has been completed on the basis of this finding.

The present invention provides a heat-sensitive recorder comprising, on a support, a heat-sensitive recording layer containing a leuco compound and an organic acidic substance capable of developing upon reaction with the leuco compound, wherein the heat-sensitive recording layer further contains a compound of the following general formula (I) or (II) as color formation-accelerator:





... (II)

10 wherein R represents an alkyl group having 1 to 4 carbon atoms, and R<sub>1</sub> and R<sub>2</sub> each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

15 Description of the Preferred Embodiments

The heat-sensitive recorder of the present invention comprises a heat-sensitive recording layer comprising a leuco compound and an organic acidic substance as a developer as the indispensable components, and a compound of the above general formula (I) or (II) as a color formation accelerator, the layer being formed on a support.

The compounds of the general formula (I) or (II) used as the color formation-accelerator in the present invention have an excellent color formation-accelerating effect and it does not impair the properties of the heat-sensitive recorder such as background density, background fog after storage and color fastness thereof.

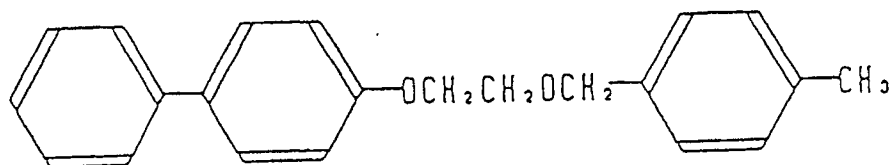
25 In the formula (I), it is preferable that R is an alkyl group having 1 to 3 carbon atoms. On the other hand, in the formula (II), it is preferable that R<sub>1</sub> and R<sub>2</sub> each represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms. It is also preferable that R<sub>1</sub> represents a hydrogen atom and R<sub>2</sub> represents an alkyl group having 1 to 3 carbon atoms.

30 From the viewpoint of the color formation-acceleration, the amount of the compound of the general formula (I) or (II) is preferably 1 to 50% by weight (hereinafter referred to as "%"), more preferably 10 to 40%, based on the total solid content of the heat-sensitive recording layers

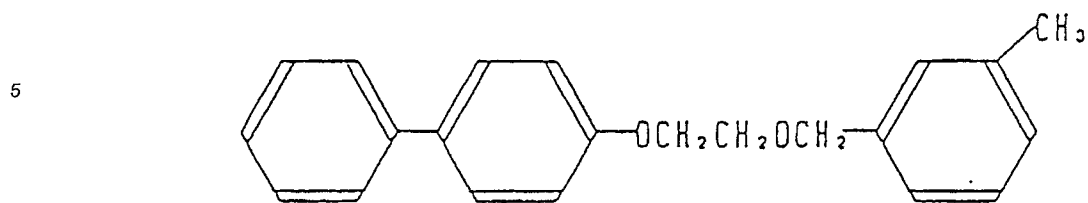
The compounds of the general formula (I) can be produced by various processes. For example, they can be produced by etherifying OH group of p-phenylphenol with ethylene chlorohydrin or ethylene oxide and then further etherifying OH group of the formed compound with an alkyl-substituted benzyl halide such as p-methylbenzyl chloride.

35 Typical examples of the compounds of the general formula (I) include the following compounds:

Compound No. 1



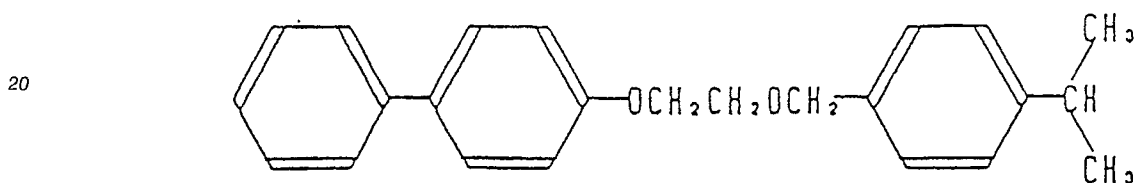
45 4-[2-(p-methylbenzyloxy)ethoxy]biphenyl,

Compound No. 2

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4-[2-(m-methylbenzyloxy)ethoxy]biphenyl, and

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Compound No. 3

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4-[2-(p-isopropylbenzyloxy)ethoxy]biphenyl.

Also the compounds of the general formula (II) can be produced by various processes. For example, they can be produced by nucleophilic reaction of a 1,4-dihalomethylbenzene such as 1,4-dichloromethylbenzene with a benzyl alcohol derivative such as p-methylbenzyl alcohol in the presence of a phase transfer catalyst such as a tetraalkylammonium halide.

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Typical examples of the compounds of the general formula (II) include the following compounds:

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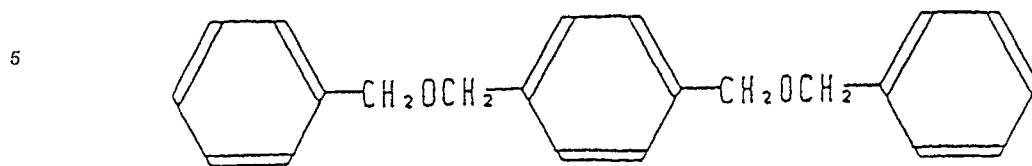
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Compound No. 21

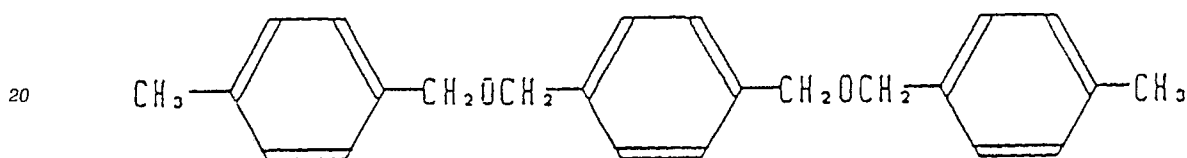


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1,4-bis(benzyloxymethyl)benzene

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Compound No. 22

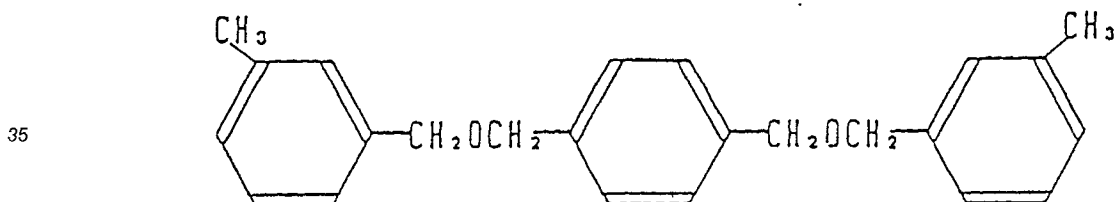


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1,4-bis(p-methylbenzyloxymethyl)benzene,

30

Compound No. 23

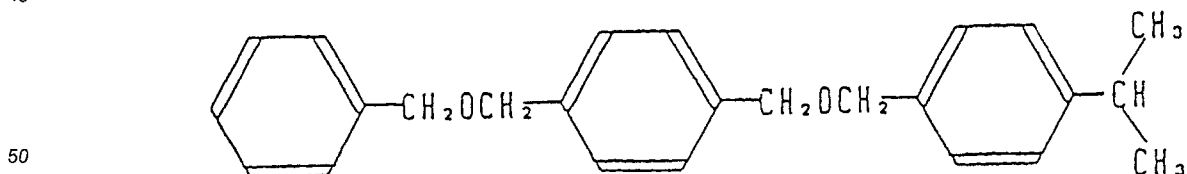


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1,4-bis(m-methylbenzyloxymethyl)benzene, and

45

Compound No. 24



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1-benzyloxymethyl-4-(p-isopropylbenzyloxymethyl)benzene.

Leuco compounds

The leuco compounds used in the present invention are colorless or light-colored substances which form a color upon reaction with the organic acidic substance. They include various derivatives such as triphenylmethane, triphenylmethane phthalide, fluoran, leuco-Auramine, diphenylmethane, phenothiazine, phenoxazine, spiropyran, indoline and indigo compound. Preferred leuco compounds include, for example,  
 5 Crystal Violet Lactone, 3-diethylamino-6-methyl-7-anilino-fluoran, 3-(N-ethyl-P-toluidino)-6-methyl-7-anilino-fluoran, 3-diethylamino-6-methyl-7-(o-, p-dimethylanilino)fluoran, 3-piperidino-6-methyl-7-anilino-fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-7-(ochloroanilino)fluoran, 3-diethylamino-7-(m-trifluoromethylanilino)fluoran, 3-diethylamino-6-methylchloro-fluoran, 3-diethylamino-6-methylfluoran, 3-(N-isoamyl-N-ethylamino)-6-methyl-7-anilino-fluoran and 3-dibutylamino-6-methyl-7-anilino-fluoran.  
 10 anilino-fluoran.

They are used either singly or in the form of a mixture of two or more of them. It is desirable that the amount of the leuco compound is 1 to 20%, preferably 5 to 15%, based on the total solid content of the heat-sensitive recording layer.

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#### Organic acidic substances

The organic acidic substances used in the present invention are substances which are solid at ambient temperature, which are molten by heating and which form a developer upon contact with the leuco  
 20 compound. They include phenolic compounds, fatty acids, aromatic carboxylic acids and esters of them.

It is desirable that the amount of the organic acidic substance used in the present invention is 1 to 50%, preferably 10 to 40%, based on the total solid content of the heat-sensitive recording layer.

The organic acidic substances include, for example, gallic acid, salicylic acid, 1-hydroxy-2-naphthoic acid, o-hydroxybenzoic acid, m-hydroxybenzoic acid, 2-hydroxy-p-toluic acid, 3,5-xyleneol, thymol, p-tert-butylphenol, 4-hydroxyphenoxide, methyl-4-hydroxybenzoate, 4-hydroxy-acetophenone,  $\alpha$ -naphthol,  $\beta$ -naphthol, catechol, resorcin, hydroquinone, 4-tert-octylcatechol, 4,4'-sec-butylidenediphenol, 2,2'-dihydroxydiphenyl, 2,2'-methylenebis(4-methyl-6-tertbutylphenol), 2,2'-bis(4-hydroxyphenyl)propane (bisphenol A), 4,4-isopropylidene-bis(2-tert-butylphenol), pyrogallol, phloroglucin, phloroglucincarboxylic acid, p-methylphenol, p-phenylphenol, 4,4'-cyclohexylidenediphenol, 4,4'-isopropylidenedicatechol, 4,4'-benzylidenediphenol, 4,4'-isopropylidenebis(2-chlorophenol), 3-phenylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 1-oxy-2-naphthoic acid, gallic acid esters, salicylic acid esters, p-hydroxybenzoic acid esters, 4-hydroxyphthalic acid esters, 2-(4-hydroxyphenyl)-2-(3'-hydroxyphenyl)propane and 4,4'-dihydroxy-3,3'-diisopropyl diphenyl-2,2'-propane. They are used either singly or in the form of a mixture of two or more of them.  
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Although the relative amounts of the leuco compound, acidic compound and color formation-accelerator of the general formula (I) or (II) are not particularly limited, the weight ratio of the leuco compound / acidic substance / color formation-accelerator is preferably 1 / (1-3) / (1-3).  
 35

A binder is used for forming the heat-sensitive recording layer in the present invention. The binder mainly comprises a water-soluble binder and it is capable of fixing fine particles of the developer dispersed therein in such a state that they are separated from one another. The binders include polyvinyl alcohol, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, polyacrylic acid, casein, gelatin, starch and derivatives of them. It is desirable that the binder is used in an amount of 1 to 35%, preferably 10 to 30%, based on the total solid content of the heat-sensitive recording layer.  
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#### Other additives

The heat-sensitive recording layer of the present invention may contain, if necessary, other additives such as inorganic or organic pigments, e.g. clay, calcium carbonate, synthetic silica, aluminum hydroxide, talc, titanium oxide and zinc oxide; waxes; antioxidants for keeping the layer stable; U. v. absorbers; various metal salts of fatty acids for inhibition of sticking; water-proofing agents for improving water resistance; phenolic resins; and surfactants.  
 50

#### Supports

The supports usable in the present invention usually include papers such as wood-free papers, coarse papers and coated papers, as well as glass fiber sheets, plastic sheets and film-laminated sheets.  
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Production of the heat-sensitive recorder

The paint for forming the heat-sensitive recording layer of the present invention is usually prepared by finely dispersing the above-described leuco compound, organic acid substance, color formation-accelerator of the above general formula (I) and/or (II) and, if necessary, additives such as the pigment and a sensitivity-regulating agent in an aqueous medium containing a binder such as polyvinyl alcohol of a suitable concentration with a ball mill or sand grinder. From the viewpoint of the color formation efficiency, it is advantageous that the components are pulverized as finely as possible. In particular, they are pulverized to a diameter of 0.5 to 3 $\mu$ m. The heat-sensitive paint thus obtained is applied to the above-described support and dried to obtain the heat-sensitive recorder of the present invention.

The coating can be conducted with an ordinary blade coater, air knife coater, bar coater, reverse roll coater or the like. The amount of the coating material for forming the heat-sensitive recording layer is not particularly limited. It is preferably 2 to 12 g/m<sup>2</sup>, more preferably 3 to 10 g/m<sup>2</sup>.

According to the present invention, there is provided the heat-sensitive recorder having a quite high image density and high practical value. The heat-sensitive recorder has also a quite excellent storability.

The following Examples will further illustrate the present invention.

## [Examples]

Synthesis Examples

The following Examples of synthesis of the compounds by no means limit the present invention.

Synthesis of 4-[2-(p-methylbenzyloxy)ethoxy]biphenyl

## (Compound No. 1)

250.0 g of p-phenylphenol, 236.5 g of ethylene chlorohydrin and 176.3 g of 95% sodium hydroxide were placed in a 1 l four-necked flask provided with a condenser, thermometer and a stirrer and the heating was started under stirring in nitrogen stream. After heating at 70 $^{\circ}$ C for 4 h, the reaction mixture was cooled to room temperature and excess ethylene chlorohydrin was distilled off under reduced pressure. 1 l of chloroform was added to the residue, an insoluble matter thus formed was removed by filtration and chloroform was distilled off under reduced pressure. The residue was recrystallized from acetone to obtain 148.0 g of 2-hydroxyethyldiphenyl ether (white crystals).

Then 100.0 g of 2-hydroxyethyldiphenyl ether produced as described above, 131.3 g of p-methylbenzyl chloride, 37.5 g of 95% sodium hydroxide and 200 ml of dimethylformamide were placed in a 500 ml four-necked flask provided with a condenser, thermometer and stirrer and they were stirred under heating at 100 $^{\circ}$ C for 3 h. After cooling to room temperature, dimethylformamide was distilled off under reduced pressure. 500 ml of toluene was added to the residue. It was washed with 200 ml of distilled water three times and dehydrated over anhydrous magnesium sulfate. The solvent was distilled off under reduced pressure. The residue was recrystallized from isopropanol to obtain 80.1 g of 4-[2-(p-methylbenzyloxy)ethoxy]biphenyl (white crystals, melting point: 85.2 $^{\circ}$ C).

The spectral analytical results of the compound were as shown below.

<sup>1</sup>H-NMR absorption spectrum [CDCl<sub>3</sub>  $\delta$  (ppm)]

2.68 (3H, s)

4.02 to 4.26 (2H, m)

4.40 to 4.63 (2H, m)

4.93 (2H, s)

7.13 to 8.00 (13H, m)

IR absorption spectrum [KBr wave length (cm<sup>-1</sup>)]

2850, 1600, 1258, 1130, 1050, 769

Synthesis of 1,4-bis(p-methylbenzyloxymethyl)benzene

(Compound No. 22)

125.0 g of p-methylbenzyl alcohol, 85.5 g of 1,4-dichloromethylbenzene, 9.85 g of trioctylmethylammonium chloride, 520 g of 45% aqueous sodium hydroxide solution and 150 ml of chlorobenzene were placed in a 1 l four-necked flask provided with a condenser, thermometer and stirrer and the heating was started under stirring in nitrogen stream. After heating at 80 °C for 4 h, the reaction mixture was cooled to room temperature. 250 ml of toluene was added to the liquid reaction mixture. An aqueous layer thus formed was taken out. The product was washed with 200 ml of distilled water three times. It was dehydrated over anhydrous magnesium sulfate and the solvent is distilled off under reduced pressure. The residue was recrystallized from ethanol to obtain 142.5 g of 1,4-bis(p-methylbenzyloxymethyl)benzene (white crystal, melting point: 97.4 °C).

The spectral analytical results of the compound were as shown below:

<sup>1</sup>H-NMR absorption spectrum [CDCl<sub>3</sub> δ (ppm)]

2.76 (6H, s)

4.91 (8H, s)

7.37 to 7.80 (12H, m)

IR absorption spectrum [KBr wave length (cm<sup>-1</sup>)]

2850, 1390, 1345, 1090, 1020, 995, 790

### Example 1

Dispersions A and B having the following compositions were prepared by dispersing the components with a paint shaker (a product to Toyo Seiki) for 16 h.

Dispersion A:	
leuco dye: 3-dibutylamino-6-methyl-7-anilino-fluoran	5 g
4-[2-(p-methylbenzyloxy)ethoxy]biphenyl (compound 1)	8 g
zinc stearate	5 g
12% polyvinyl alcohol solution	35 g
water	47 g
Dispersion B:	
bisphenol A	15 g
zinc stearate	3 g
12% polyvinyl alcohol solution	35 g
water	47 g

100 g of the Dispersion A, 100 g of the Dispersion B, 50 g of 12% polyvinyl alcohol solutions 15 g of synthetic silica P-832 (produced by Mizusawa Kagaku Co.) and 60 g of water were mixed together by stirring to form a coating solution. The coating solution was spread on the surface of a 50 g/m<sup>2</sup> wood-free paper with a wire bar so as to form a 8 g/m<sup>2</sup> (on dry basis) of a coating film to obtain a heat-sensitive recording paper.

### Example 2

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 3-butylamino-6-methyl-7-anilino-fluoran used as a component of the Dispersion A was replaced with 3-(N-isoamyl-N-ethylamino)-6-methyl-7-anilino-fluoran.

### Example 3

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl used as a component of the Dispersion A was replaced with 4-[2-

m-methylbenzyloxy)ethoxy]biphenyl (Compound 2).

#### Example 4

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A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl used as a component of the Dispersion A was replaced with 4-[2-(p-isopropylbenzyloxy)ethoxy]biphenyl (Compound 3).

10

#### Example 5

A heat sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl used as a component of the Dispersion A was replaced with 1,4-bis(p-methylbenzyloxymethyl)benzene (Compound 22).

15

#### Example 6

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl used as a component of the Dispersion A was replaced with 1,4-bis(m-methylbenzyloxymethyl)benzene (Compound 23).

20

#### Example 7

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl used as a component of the Dispersion A was replaced with 1-benzyloxymethyl-4-(p-isopropylbenzyloxymethyl) benzene (Compound 24).

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#### Comparative Example 1

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl (Compound 1) used as a component of the Dispersion A was omitted.

35

#### Comparative Example 2

40

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl (Compound 1) used as a component of the Dispersion A was replaced with stearamide.

45

#### Comparative Example 3

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl (Compound 1) used as a component of the Dispersion A was replaced with p-benzylbiphenyl.

50

#### Comparative Example 4

A heat-sensitive recording paper was produced in the same manner as that of Example 1 except that 4-[2-(p-methylbenzyloxy) ethoxy]biphenyl (Compound 1) was replaced with 2-benzyloxynaphthalene.

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The heat-sensitive recording papers produced in the above-described Examples and Comparative Examples were surface-treated with a test super calender so that the recording surface thereof would have

a Bekk smoothness of 500 sec. The following properties of them were examined to obtain the results shown in Table 1.

#### 5 Coloring-initiation temperature

A heated block was pushed against the heat-sensitive surface of each paper (200 g/cm<sup>2</sup>, 5 sec). The coloring initiation temperature was shown in terms of the temperature at which the color density in the colored portion was 0.2.

10

#### Image density

15 Solid printing was conducted with a commercial thermal head (KFT-216-8 MPD1; a product of Kyoto Ceramic Co., Ltd.) under conditions comprising a printing electric power of 0.70 W/dot, printing pulse time of 0.4 ms and printing pulse period of 5.0 ms. The background density and image density were determined.

#### Storage stability

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The background density and image density after storage in a dry constant-temperature room at 60 °C for 24 h were examined.

Table 1

25

		Coloring initiation temperature (°C)	Background density	Image density	Storage stability	
					Background density	Image density
Example	1	75	0.02	1.22	0.04	1.17
	2	71	0.04	1.26	0.07	1.21
	3	75	0.03	1.21	0.04	1.13
	4	75	0.03	1.21	0.04	1.14
	5	75	0.03	1.20	0.04	1.13
	6	74	0.03	1.20	0.04	1.14
	7	75	0.02	1.20	0.04	1.15
Comparative Example	1	89	0.02	0.75	0.03	0.61
	2	76	0.03	0.89	0.06	0.77
	3	75	0.03	1.05	0.05	1.02
	4	79	0.02	1.09	0.05	1.06

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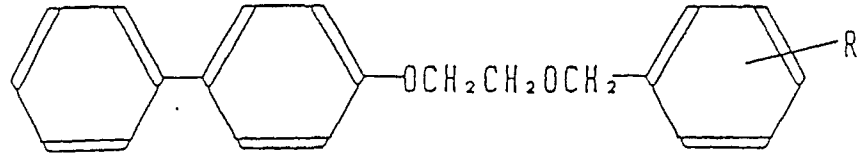
It is apparent from the results shown in Table 1 that the heat-sensitive recorders produced with the compound of general formula (I) or (II) in Examples 1 to 7 have an excellent image density and a quite excellent storage stability.

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#### Claims

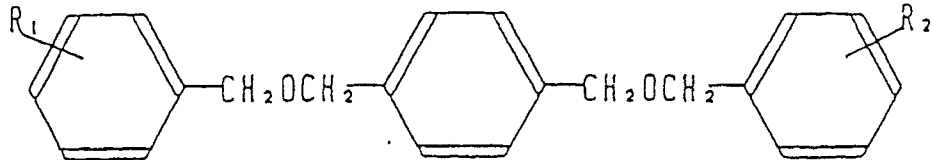
1. A heat-sensitive recorder comprising, on a support, a heat-sensitive recording layer containing a leuco compound and an organic acidic substance capable of developing upon reaction with the leuco compound, wherein the heat-sensitive recording layer further contains a compound of the following general formula (I) or (II):

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... (I)



10

15

... (II)

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wherein R represents an alkyl group having 1 to 4 carbon atoms, and R<sub>1</sub> and R<sub>2</sub> each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. The heat-sensitive recorder according to claim 1 wherein R in the general formula (I) is an alkyl group having 1 to 3 carbon atoms.

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3. The heat-sensitive recorder according to claim 1 wherein R<sub>1</sub> and R<sub>2</sub> in the general formula (II) are each a hydrogen atom.

4. The heat-sensitive recorder according to claim 1 wherein R<sub>1</sub> and R<sub>2</sub> in the general formula (II) are each an alkyl group having 1 to 3 carbon atoms.

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5. The heat-sensitive recorder according to claim 1 wherein R<sub>1</sub> in the general formula (II) is a hydrogen atom and R<sub>2</sub> is an alkyl group having 1 to 3 carbon atoms.

6. The heat-sensitive recorder according to any one of claims 1 to 5 which contains 1 to 50% by weight, based on the total solid content of the heat-sensitive recording layer, of a compound of the general formula (I) or (II).

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7. The heat-sensitive recorder according to any one of claims 1 to 6 which contains 1 to 20% by weight, based on the total solid content of the heat-sensitive recording layer, of the leuco compound.

8. The heat-sensitive recorder according to any one of claims 1 to 7 which contains 1 to 50% by weight, based on the total solid content of the heat-sensitive recording layer, of an organic acidic substance.

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